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Simple Models and Electron Microscopies Describing Aggregates of Metal Nanoparticles

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A dissertation
submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

University of Washington

2018

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Abstract

Simple Models and Electron Microscopies Describing Aggregates of Metal Nanoparticles

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This sample dissertation is an aid to students who are attempting to format their theses with \LaTeX , a sophisticated text formatter widely used by mathematicians and scientists everywhere.

- It describes the use of a specialized macro package developed specifically for thesis production at the University. The macros customize \LaTeX for the correct thesis style, allowing the student to concentrate on the substance of his or her text.¹
- It demonstrates the solutions to a variety of formatting challenges found in thesis production.
- It serves as a template for a real dissertation.

¹See Appendix A to obtain the source to this thesis and the class file.

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GLOSSARY

ARGUMENT: replacement text which customizes a \LaTeX macro for each particular usage.

BACK-UP: a copy of a file to be used when catastrophe strikes the original. People who make no back-ups deserve no sympathy.

CONTROL SEQUENCE: the normal form of a command to \LaTeX .

DELIMITER: something, often a character, that indicates the beginning and ending of an argument. More generally, a delimiter is a field separator.

DOCUMENT CLASS: a file of macros that tailors \LaTeX for a particular document. The macros described by this thesis constitute a document class.

DOCUMENT OPTION: a macro or file of macros that further modifies \LaTeX for a particular document. The option `[chapternotes]` constitutes a document option.

FIGURE: illustrated material, including graphs, diagrams, drawings and photographs.

FONT: a character set (the alphabet plus digits and special symbols) of a particular size and style. A couple of fonts used in this thesis are twelve point roman and *twelve point roman slanted*.

FOOTNOTE: a note placed at the bottom of a page, end of a chapter, or end of a thesis that comments on or cites a reference for a designated part of the text.

FORMATTER: (as opposed to a word-processor) arranges printed material according to instructions embedded in the text. A word-processor, on the other hand, is normally controlled by keyboard strokes that move text about on a display.

\LaTeX : simply the ultimate in computerized typesetting.

MACRO: a complex control sequence composed of other control sequences.

PICA: an archaic unit of length. One pica is twelve points and six picas is about an inch.

POINT: a unit of length. 72.27 points equals one inch.

ROMAN: a conventional printing typestyle using serifs. the decorations on the ends of letter strokes. This thesis is set in roman type.

RULE: a straight printed line; e.g., _____.

SERIF: the decoration at the ends of letter strokes.

TABLE: information placed in a columnar arrangement.

THESIS: either a master's thesis or a doctoral dissertation. This document also refers to itself as a thesis, although it really is not one.

ACKNOWLEDGMENTS

The author wishes to express sincere appreciation to mom and dad, research group, community community community.

DEDICATION

to my queens, Barbra Streisand and Ruth Bader Ginsburg

Chapter 1

INTRODUCTION

A brief history of plasmonics. Contextualization of my goals, like catalysis and negative-index materials. Cool applications.

When one thinks of a metal, a few images come to mind: electrical wires that power modern technology or a reflection in a mirror. These images arise from the understanding that metals are particularly good conductors; the conduction electrons in metals are generally free to move about uninhibited. This conductivity is what makes mirrors possible. The conduction electrons in a metal will rearrange themselves to screen incoming electric fields, such as those from light. Of course, in reality, no metals are perfect conductors. This means that light actually can penetrate metal up to a distance known as the metal's skin-depth, on the order of 10-100 nanometers. Now, imagine a piece of metal about that size (a nanoparticle is to the reader as the reader is to Earth); an incoming light wave can penetrate the nanoparticle entirely, perfectly polarizing its conduction electrons. For the most part, the electrons are unable to leave the nanoparticle, so they collect on the surface. When the field is removed, the electrons drift back to their equilibrium positions, overshoot, and swing to the opposite surface. This collective and coherent oscillation of the electron plasma is known as a localized surface plasmon resonance (LSPR). For most metal nanoparticles, the LSPR frequency is somewhere between the near IR and the near UV.

Though first predicted in 1952 by Bohm and Pines, LSPRs have had great impact on arts and culture since the Gothic movements of Western Europe. The vibrant colors of stained glass are the result of colloidal gold nanoparticles suspended in the glass. The color depends on the particle size and density. But why? Well, that's part of what we're going to learn in this introduction: why the size and aggregation scheme of nanoparticles affect their

optical properties. To do this, we'll need to understand the optical properties of individual nanoparticles and investigate how nanoparticles interact in aggregates. Not only will this explain the phenomenon responsible for the colors of stained glass, but it will also inform the description and characterization of metal nanoparticle aggregates that make up the main text of this thesis.

1.1 *LSPRs as Harmonic Oscillators*

In order to understand the harmonic oscillator dynamics of a metal nanosphere, we must consider its polarizability,

$$\alpha(\omega) = a^3 \frac{\ell(\varepsilon(\omega) - \varepsilon_b)}{\ell(\varepsilon(\omega) + \varepsilon_b) + \varepsilon_b}. \quad (1.1)$$

This is the frequency-dependent polarizability from the Clausius-Mossotti relation, defined by frequency-dependent dielectric function

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (1.2)$$

where $\omega_p^2 = 4\pi n e^2 / m$ is the plasma frequency and γ is the bulk damping rate. Plugging Equation 1.2 into Equation 1.1 and doing some algebra, we can coax the polarizability into a slightly more useful form. We will also, for now, set $\ell = 1$ because we are only considering the dipole response of the sphere, and we will also set $\varepsilon_b = 1$ because we are concerned only with spheres in vacuum.

$$\alpha(\omega) = a^3 \left[\frac{(\omega^2 + i\gamma\omega) \left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \right) - \omega_{sp}^2}{\omega^2 + i\gamma\omega - \omega_{sp}^2} \right] \quad (1.3)$$

Here, $\omega_{sp}^2 = \omega_p^2 / \varepsilon_\infty + 2$ is the surface plasmon frequency for a dipole. Now that we have this rather complicated-looking function of frequency, we want to know a bit about the behavior of the polarizability in the time domain. In order to do that, we're going to Fourier transform the polarizability. However, the denominator of the polarizability contains two

poles, so we're going to have to do a contour integral using the residue theorem to actually compute the Fourier transform. Equation 1.3 has poles at $\omega = -i\gamma/2 \pm \sqrt{\omega_{\text{sp}}^2 - \gamma^2/4}$. We are trying to find

$$\alpha(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \alpha(\omega) e^{i\omega t} = 2\pi i \sum \text{Res} \quad (1.4)$$

Because it has two poles, the integrand in Equation 1.4 has two residues

$$R_{\pm} = \pm \frac{1}{2\pi} \frac{\omega_{\text{sp}}^2 \left(\frac{\varepsilon_{\infty}-1}{\varepsilon_{\infty}+2} - 1 \right)}{2\sqrt{\omega_{\text{sp}}^2 - \gamma^2/4}} e^{-\gamma t/2} e^{\pm i\sqrt{\omega_{\text{sp}}^2 - \gamma^2/4}t} \quad (1.5)$$

Plugging each of the residues into the residue theorem, doing some algebra, and remembering that $2i\sin(\phi) = e^{i\phi} - e^{-i\phi}$, results in the following expression for the polarizability.

$$\alpha(t) = a^3 \left(\frac{3}{\varepsilon_{\infty} + 2} \right) \frac{\omega_{\text{sp}}^2}{\sqrt{\omega_{\text{sp}}^2 - \gamma^2/4}} e^{-\gamma t/2} \sin(\sqrt{\omega_{\text{sp}}^2 - \gamma^2/4}t) \quad (1.6)$$

Equation 1.6 has two important pieces. The first is the sinusoidal term, oscillating at frequency $\sqrt{\omega_{\text{sp}}^2 - \gamma^2/4}$. The second is the exponential term, decaying with width $\gamma/2$. These two terms show that a plasmon has time dynamics consistent with a harmonic oscillator. Now that we understand how one dipole plasmon behaves, let us move on to considering multiple.

1.2 Multiple Metal Nanoparticles

Let's talk about plasmon hybridization theory. I can make a really wonderful analogy for the chemists in the room: this is basically molecular orbital theory. What do I mean by that? Well, take any two atomic orbitals. Maybe two s-orbitals on two hydrogen atoms. Bring them close to each other. What happens? They mix - two atomic orbitals become two molecular orbitals, each with different properties. The lower energy mode with significant overlap is called the bonding (σ) orbital. The higher-energy mode with no overlap is called the anti-bonding (σ^*) orbital. Pairs of LSPRs behave similarly. When brought close to

each other, they hybridize and produce new normal modes, one lower energy and one higher energy. If one LSPR is a harmonic oscillator, then two or more can be treated like a system of coupled harmonic oscillators. Let's look at the case where we have only two LSPRs with fixed orientations along the direction of displacement (maybe include a diagram here, smarty pants). Write down the Hamiltonian, write Hamilton's equations, write Newton's equations, solve the system of equations.

1.3 List of publications

1. Alpha-terpinene 2. Imaging hybridization 3. AuPt 4. Magnetic Hybridization 5. Landau damping 6. Tunable magnetic plasmons 7? SEELS?

Chapter 2

PLASMON HYBRIDIZATION: HISTORY AND THEORY

Lit review of plasmon hybridization. Chemical analogies. In-depth explanation of the coupled dipole approximation (CDA). In-depth explanation of how the CDA varies in the quasistatic limit vs. fully retarded.

The \TeX formatting program is the creation of Donald Knuth of Stanford University. It has been implemented on nearly every general purpose computer and produces exactly the same copy on all machines.

2.1 What is it; why is it spelled that way; and what do really long section titles look like in the text and in the Table of Contents?

\TeX is a formatter. A document's format is controlled by commands embedded in the text. \LaTeX is a special version of \TeX —preloaded with a voluminous set of macros that simplify most formatting tasks.

\TeX uses *control sequences* to control the formatting of a document. These control sequences are usually words or groups of letters prefaced with the backslash character (\backslash). For example, Figure 2.1 shows the text that printed the beginning of this chapter. Note the control sequence $\backslash\text{chapter}$ that instructed \TeX to start a new chapter, print the title, and make an entry in the table of contents. It is an example of a macro defined by the \LaTeX macro package. The control sequence $\backslash\text{TeX}$, which prints the word \TeX , is a standard macro from the *\TeX book*. The short control sequence $\backslash\backslash$ in the title instructed \TeX to break the title line at that point. This capability is an example of an extension to \LaTeX provided by the *uwthesis* document class.

Most of the time \TeX is simply building paragraphs from text in your source files. No

```
\chapter{A Brief\Description of \TeX}
```

```
The \TeX\ formatting program is the creation of  
Donald Knuth of Stanford University.
```

Figure 2.1: The beginning of the Chapter II text

control sequences are involved. New paragraphs are indicated by a blank line in the input file. Hyphenation is performed automatically.

2.2 *TEXbooks*

The primary reference for L^AT_EX is Lamport's second edition of the *L^AT_EX User's Guide*[?]. It is easily read and should be sufficient for thesis formatting. See also the *L^AT_EX Companion*[?] for descriptions of many add-on macro packages.

Although unnecessary for thesis writers, the *TEXbook* is the primary reference for T_EXsperts worldwide.

2.3 *Mathematics*

The thesis class does not expand on T_EX's or L^AT_EX's comprehensive treatment of mathematical equation printing.¹ The *TEXbook*[?], *L^AT_EX User's Guide*[?], and *The L^AT_EX Companion*[?] thoroughly cover this topic.

¹Although many T_EX-formatted documents contain no mathematics except the page numbers, it seems appropriate that this paper, which is in some sense about T_EX, ought to demonstrate an equation or two. Here then, is a statement of the *Nonsense Theorem*.

Assume a universe E and a symmetric function $\$$ defined on E , such that for each $\yy there exists a $\overline{\$^{yy}}$, where $\$^{yy} = \overline{\overline{\$^{yy}}}$. For each element i of E define $\mathcal{S}(i) = \sum_i \$^{yy} + \overline{\$^{yy}} + 0$. Then if \mathcal{RR} is that subset of E where $1 + 1 = 3$, for each i

$$\lim_{\$ \rightarrow \infty} \int \mathcal{S} di = 0, \text{ if}$$

$i \notin \mathcal{RR}; \infty, i \in \mathcal{RR}$.

2.4 *Languages other than English*

Most L^AT_EX implementations at the University are tailored for the English language. However, L^AT_EX will format many other languages. Unfortunately, this author has never been successful in learning more than a smattering of anything other than English. Consult your department or the Tex Users Group.

`http://tug.org/`,

for assistance with non-English formatting.

Unusual characters can be defined via the font maker METAFONT (documented by Knuth[?]). The definitions are not trivial. Students who attempt to print a thesis with custom fonts may soon proclaim,

“ἀποθανεῖν θέλω.”

Chapter 3

PAPER 1: MAGNETIC PLASMONS

This chapter describes the `uwthesis` class (`uwthesis.cls`, version dated 2014/11/13) in detail and shows how it was used to format the thesis. A working knowledge of Lamport's `LATEX` manual[?] is assumed.

3.1 *The Control File*

The source to this sample thesis is a single file only because ease of distribution was a concern. You should not do this. Your task will be much easier if you break your thesis into several files: a file for the preliminary pages, a file for each chapter, one for the glossary, and one for each appendix. Then use a control file to tie them all together. This way you can edit and format parts of your thesis much more efficiently.

Figure 3.1 shows a control file that might have produced this thesis. It sets the document style, with options and parameters, and formats the various parts of the thesis—but contains no text of its own.

The first section, from the `\documentclass` to the `\begin{document}`, defines the document class and options. This sample thesis specifies the `proquest` style, which is now required by the Graduate School and is the default. Two other, now dated, other styles are available: `twoside`, which is similar but produces a wider binding margin and is more suitable for paper printing; and `oneside`, which is really old fashioned. This sample also specified a font size of 11 points. Possible font size options are: `10pt`, `11pt`, and `12pt`. Default is 12 points, which is the preference of the Graduate School. If you choose a smaller size be sure to check with the Graduate School for acceptability. The smaller fonts can produce very small sub and superscripts.

```

% LaTeX thesis control file

\documentclass [11pt, proquest]{uwthesis}[2014/11/13]

\begin{document}

% preliminary pages
%
\prelimpages
\include{prelim}

% text pages
%
\textpages
\include{chap1}
\include{chap2}
\include{chap3}
\include{chap4}

% bibliography
%
\bibliographystyle{plain}
\bibliography{thesis}

% appendices
%
\appendix
\include{appxa}
\include{appxb}

\include{vita}
\end{document}

```

Figure 3.1: A thesis control file (`thesis.tex`). This file is the input to \LaTeX that will produce a thesis. It contains no text, only commands which direct the formatting of the thesis.

Include most additional formatting packages with `\usepackage`, as describe by Lamport[?]. The one exception to this rule is the `natbib` package. Include it with the `natbib` document option.

Use the `\includeonly` command to format only a part of your thesis. See Lamport[?, sec. 4.4] for usage and limitations.

3.2 The Text Pages

A chapter is a major division of the thesis. Each chapter begins on a new page and has a Table of Contents entry.

3.2.1 Chapters, Sections, Subsections, and Appendices

Within the chapter title use a `\\` control sequence to separate lines in the printed title (recall Figure 2.1.). The `\\` does not affect the Table of Contents entry.

Format appendices just like chapters. The control sequence `\appendix` instructs `LATEX` to begin using the term ‘Appendix’ rather than ‘Chapter’.

Specify sections and subsections of a chapter with `\section` and `\subsection`, respectively. In this thesis chapter and section titles are written to the table of contents. Consult Lamport[?, pg. 176] to see which subdivisions of the thesis can be written to the table of contents. The `\\` control sequence is not permitted in section and subsection titles.

3.2.2 Footnotes

Footnotes format as described in the `LATEX` book. You can also ask for end-of-chapter or end-of-thesis notes. The thesis class will automatically set these up if you ask for the document class option `chapternotes` or `endnotes`.

If selected, `chapternotes` will print automatically. If you choose `endnotes` however you must explicitly indicate when to print the notes with the command `\printendnotes`. See the style guide for suitable endnote placement.

3.2.3 *Figures and Tables*

Standard L^AT_EX figures and tables, see Lamport[?, sec. C.9], normally provide the most convenient means to position the figure. Full page floats and facing captions are exceptions to this rule.

If you want a figure or table to occupy a full page enclose the contents in a **fullpage** environment. See figure 3.2.

Facing pages

Facing page captions are an artifact of traditional, dead-tree printing, where a left-side (even) page faces a right-side (odd) page.

In the **twoside** style, a facing caption is full page caption for a full page figure or table and should face the illustration to which it refers. You must explicitly format both pages. The caption part appears on an even page (left side) and the figure or table comes on the following odd page (right side). Enclose the float contents for the caption in a **leftfullpage** environment, and enclose the float contents for the figure or table in a **fullpage** environment. The first page (left side) contains the caption. The second page (right side) could be left blank. A picture or graph might be pasted onto this space. See figure 3.2.

You can use these commands with the **proquest** style, but they have little effect on online viewing.

3.2.4 *Horizontal Figures and Tables*

Figures and tables may be formatted horizontally (a.k.a. landscape) as long as their captions appear horizontal also. L^AT_EX will format landscape material for you.

Include the **rotating** package

```
\usepackage[figuresright]{rotating}
```

and read the documentation that comes with the package.

Figure 3.3 is an example of how a landscape table might be formatted.

```

\begin{figure}[p]% the left side caption
  \begin{leftfullpage}
    \caption{ . . . }
  \end{leftfullpage}
\end{figure}
\begin{figure}[p]% the right side space
  \begin{fullpage}
    . . .
    ( note.. no caption here )
  \end{fullpage}
\end{figure}

```

Figure 3.2: This text would create a double page figure in the two-side styles.

```

\begin{sidewaystable}
  ...
  \caption{ . . . }
\end{sidewaystable}

```

Figure 3.3: This text would create a landscape table with caption.

3.2.5 Figure and Table Captions

Most captions are formatted with the `\caption` macro as described by Lamport[?, sec. C.9]. The `uwthesis` class extends this macro to allow continued figures and tables, and to provide multiple figures and tables with the same number, e.g., 3.1a, 3.1b, etc.

To format the caption for the first part of a figure or table that cannot fit onto a single page use the standard form:

```
\caption[toc]{text}
```

To format the caption for the subsequent parts of the figure or table use this caption:

```
\caption(-){(continued)}
```

It will keep the same number and the text of the caption will be *(continued)*.

To format the caption for the first part of a multi-part figure or table use the format:

```
\caption(a)[toc]{text}
```

The figure or table will be lettered (with ‘a’) as well as numbered. To format the caption for the subsequent parts of the multi-part figure or table use the format:

```
\caption(x){text}
```

where x is b, c, The parts will be lettered (with ‘b’, ‘c’, ...).

3.2.6 Line spacing

Normally line spacing will come out like it should. However, the ProQuest style allows single spacing in certain situations: figure content, some lists, and etc. Use `\uwsinglespace` to switch to single spacing within a `\begin{}` and `\end{}` block. The code examples in this document does this.

3.3 The Preliminary Pages

These are easy to format only because they are relatively invariant among theses. Therefore the difficulties have already been encountered and overcome by L^AT_EX and the thesis document classes.

Start with the definitions that describe your thesis. This sample thesis was printed with the parameters:

```
\Title{The Suitability of the \LaTeX\ Text Formatter\\
      for Thesis Preparation by Technical and\\
      Non-technical Degree Candidates}
\Author{Jim Fox}
\Program{IT Infrastructure}
\Year{2012}
```

```

\Chair{Name of Chairperson}{title}{Chair's department}
\Signature{First committee member}
\Signature{Next committee member}
\Signature{etc}

```

Use two or more `\Chair` lines if you have co-chairs.

3.3.1 Copyright page

Print the copyright page with `\copyrightpage`.

3.3.2 Title page

Print the title page with `\titlepage`. The title page of this thesis was printed with

```

\titlepage

```

You may change default text on the title page with these macros. You will have to redefine `\Degreetext`, for instance, if you're writing a Master's thesis instead of a dissertation.¹

```

\Degree{degree name} defaults to "Doctor of Philosophy"
\School{school name} defaults to "University of Washington"
\Degreetext{degree text} defaults to "A dissertation submitted ..."
\textofCommittee{committee label} defaults to "Reading Committee:"
\textofChair{chair label} defaults to "Chair of the Supervisory Committee:"

```

These definitions must appear before the `\titlepage` command.

¹If you use these they can be included with the other information before `\copyrightpage`.

3.3.3 *Abstract*

Print the abstract with `\abstract`. It has one argument, which is the text of the abstract. All the names have already been defined. The abstract of this thesis was printed with

```
\abstract{This sample . . . ‘real’ dissertation.}
```

3.3.4 *Tables of contents*

Use the standard L^AT_EX commands to format these items.

3.3.5 *Acknowledgments*

Use the `\acknowledgments` macro to format the acknowledgments page. It has one argument, which is the text of the acknowledgment. The acknowledgments of this thesis was printed with

```
\acknowledgments{The author wishes . . . {\it il miglior fabbro}.\par}}
```

3.3.6 *Dedication*

Use the `\dedication` macro to format the dedication page. It has one argument, which is the text of the dedication.

3.3.7 *Vita*

Use the `\vita` macro to format the curriculum vitae. It has one argument, which chronicles your life’s accomplishments.

Note that the Vita is not really a preliminary page. It appears at the end of your thesis, just after the appendices.

Chapter 4

PAPER 2: PRISMS

From a given source T_EX will produce exactly the same document on all computers and, if needed, on all printers. *Exactly the same* means that the various spacings, line and page breaks, and even hyphenations will occur at the same places.

How you edit your text files and run L^AT_EX varies from system to system and depends on your personal preference.

4.1 *Running*

The author is woefully out of his depth where T_EX on Windows is concerned. Google would be his resource. On a linux system he types

```
$ pdflatex uwthesis
```

and it generally works.

4.2 *Printing*

All implementations of T_EX provide the option of **pdf** output, which is all the Graduate School requires. Even if you intend to print a copy of your thesis create a **pdf**. It will print most anywhere.

Appendix A

The `uwthesis` class file, `uwthesis.cls`, contains the parameter settings, macro definitions, and other \TeX commands which allow \LaTeX to format a thesis. The source to the document you are reading, `uwthesis.tex`, contains many formatting examples which you may find useful. The bibliography database, `uwthesis.bib`, contains instructions to Bib \TeX to create and format the bibliography. You can find the latest of these files on:

- My page.

`http://staff.washington.edu/fox/tex/uwthesis.html`

- CTAN

`http://tug.ctan.org/tex-archive/macros/latex/contrib/uwthesis/`

(not always as up-to-date as my site)

VITA

Jim Fox is a Software Engineer with IT Infrastructure Division at the University of Washington. His duties do not include maintaining this package. That is rather an avocation which he enjoys as time and circumstance allow.

He welcomes your comments to `fox@uw.edu`.